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EFFECTS OF POND CHARACTERISTICS ON BIOTIC EXPOSURES

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16. ABSTRACT

Different aquatic communities, although apparently equivalent, can exhibit a variety of responses when challenged with the same initial total toxicant concentration. Differences in realized actual exposure concentrations can result from differences in physical morphology, water and sediment chemistry, and physical transport processes. Seasonal differences in climatology and biological community structure also alter ecosystem responses. Simulation models and comparative studies provide methods for extrapolation.

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EFFECTS OF POND CHARACTERISTICS ON BIOTIC EXPOSURES

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Abstract--Different aquatic communities, though apparently equivalent, can exhibit a variety of responses when challenged with the same initial total toxicant concentration. Differences in realized actual exposure concentrations can result from differences in physical morphometry, water and sediment chemistry, and physical transport processes. Seasonal differences in climatology and biological community structure also alter ecosystem responses. Simulation models and comparative studies provide methods for extrapolation.

Keywords--Mathematical models, Aquatic ecosystems, Pyrethroids, Fenvalerate

INTRODUCTION

A variety of pond geometries, water and sediment compositions, and biota have been used in mesocosm investigations of the chemical fate and ecological effects of pesticides (Voshell 1990). Many of these studies are executed to produce evidence to support registration of pesticides with the U.S. Environmental Protection Agency (EPA) as required by FIFRA, the Federal Insecticide, Fungicide, and Rodenticide Act. The EPA guidance document for such studies (Touart 1988, Touart and Slimak 1989) requires that the ponds used for mesocosm studies be large enough and productive enough to support a fish population, but does not specify water chemistry or physical properties in detail. For comparing results among studies, it would be useful to have tools to extrapolate among mesocosms of different types, and for extrapolation from mesocosms to larger natural bodies of water--farm ponds, lakes, and rivers.

We conducted sensitivity analyses on a model synthetic pyrethroid in three ponds under different conditions of organic carbon content of the benthic sediments, quantities of suspended particulates in the water column, and empirical dispersion coefficients used to describe transport across the benthic boundary layer. In the sensitivity analyses, the greatest contrasts were observed between a shallow mesocosm with rich organic (10% carbon) sediments and a farm pond with low (1%) organic carbon sediments. These environments were then used to explore transport, transformation, and contamination of the aquatic food chain by the model chemical in more realistic agricultural loading scenarios. In the sensitivity study, inputs were scaled to provide an initial concentration of 1 µg/L; in the agricultural loadings, inputs were scaled to provide an initial concentration of 1.1 µg/L in the water column.

MATERIALS AND METHODS

Model pyrethroid

We constructed a model synthetic pyrethroid insecticide exhibiting the properties given in Table 1. Our literature analysis was based on fenvalerate (α-cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate (IUPAC), CAS 51630-58-1, trade names Sumicidin, Pydrin, Belmark, Ectrin, Asana), a broad-spectrum insecticide with proposed application rates of 55 to 224 g ai/ha (Bennett et al. 1983). Unfortunately, the range of published values for critical

physical and chemical properties was too large for us to regard the model pyrethroid as incontrovertibly representing fenvalerate as actually manufactured. For example, published primary measurements of the octanol:water partition coefficient (expressed as log KOW) span a range from 4.42 to 6.2 (Table 1). Because KOW is a critical parameter for evaluating the environmental behavior of xenobiotics, a potential error of two orders of magnitude is unacceptable for reliable environmental studies. In what follows, our model pyrethroid will be indicated by italics as *fenvalerate*; we indicate the insecticide used for physical model studies and laboratory investigations as unitalicized "fenvalerate." It should be noted, however, that the conclusions drawn from our mathematical model studies are not dependent on the exact chemistry of fenvalerate.

Our studies were conducted using PIRANHA, a computer-based tool kit for conducting risk assessments of synthetic chemicals (Burns et al. 1990). We first evaluated the effects of pond characteristics on the distribution of a model surface load, scaled to give an initial total concentration (sum of chemical dissolved in aqueous phase, complexed with dissolved organic carbon (DOC), and sorbed to suspended particulate matter) in the water column of 1 µg/L. Following that, we developed realistic agricultural loadings using the PRZM model (Bird 1990a, Carsel et al. 1984) and contrasted a shallow mesocosm and a farm pond of differing bottom type. Finally, we explored some of the differing conclusions to be drawn from the uncertainty in the chemical literature.

Simulated environments

The pond characteristics we varied were size, carbon content of benthic sediment, and the empirical dispersion coefficient used to characterize transport of *fenvalerate* across the benthic boundary layer. The characteristics of the ponds were derived from literature values, and designed to include a range from experimental mesocosms to small constructed farm ponds. The dimensions of the small mesocosm (5 by 5 m plan area, 1 m deep) were selected from Voshell's (1990) discussion of Hill (1985). The dimensions of the shallow mesocosm were taken from the 0.1 ha plan area, 700 m^3 volume ponds described by Fairchild et al. (1991). The dimensions of the farm pond were selected to be representative of those in the Southeastern United States.

Farm ponds in the southeastern tier of the United States range in size from 0.20 ha (half-acre) ponds built by a single farmer to ponds as large as 20 ha (50 acres) built by several farmers

as a group project. A U.S. Soil Conservation Service (United States Study Commission 1960) farm pond inventory (county-by-county survey of South Carolina, Georgia, Florida, and Alabama) found that the average size of the 33,013 farm ponds in the region in 1960 was 1.4 ha (Table 2); the 1 ha pond used in this study is thus fairly typical of the region. Many ponds in the region are multi-purpose; the inventory found 76% used for fish management, 13% for irrigation, and 48% for farmstead uses (stock watering and water used in farm buildings) (U.S. Study Commission 1960). The Soil Conservation Service (1982) recommends a minimum depth of 6 to 7 feet (2 m) for ponds in the region.

Table 3 lists the pond properties that were constant in all the ponds, and Table 4 lists the properties varied for each pond type. The organic carbon content of benthic sediments was taken as 1%, 3%, and 10% of dry weight. One review of sediment characteristics from a variety of freshwater sites (Hassett et al. 1980) yielded values ranging from a low of 0.72 (EPA-6 from Antelope Creek in the impoundment behind Big Bend Dam on the Missouri River) to a high of 2.38% (EPA-23 from Crane Lake Sanganois Wildlife Refuge). The pond mesocosms operated by the U.S. Fish and Wildlife Service at Columbia, Missouri, have been reported to have sediments with 3% organic carbon (Fairchild et al. 1991). Considerably higher carbon contents, often about 10%, with a range of 5% to 14%, have been reported in fish pond sediments--the largest value, 27.8%, being found in a *Phragmitetum* accumulation area (Dykyjova and Ulehlova 1978).

Suspended sediment concentrations were set at values of 3, 30, and 300 mg/L based on values reported for lakes and reservoirs. In Tuttle Creek Reservoir, suspended particulates varied from 80 to 200 mg/L (Marzolf 1984). In a very shallow lake (1.35 m depth) in which sediments are resuspended by wind action, the suspended matter occasionally exceeded 300 mg/L (Poltz 1980). In Lake Balaton, suspended solids varied from 6.0 to 20.4 mg/L (Biro 1984). Because the small ponds considered here have little wind fetch and thus might be less subject to wind mixing than lakes, we assume that the least quantity of suspended sediments could be less than that reported for larger bodies of water.

Based on the review published with the EXAMS model (Burns et al. 1982), the dispersion coefficient used as an empirical model of transport across the benthic boundary layer was set at

1.0, 2.9, and 7.5 (all $\times 10^{-5}$) m^2h^{-1}. This range assumes the presence of an active benthic infauna and some physical (wind) effects (at the high end). By contrast, purely diffusive exchange would give an dispersion constant of about 10^{-6} m^2h^{-1}, and near-shore maritime turbulence a value of about 10^{-4} m^2h^{-1}.

Experimental mesocosms tend to be smaller than typical farm ponds because the EPA experimental protocol requires a minimum of 12 units--larger ponds require more real estate, would be more expensive to construct and maintain, and might be more difficult to sample adequately. The pond sizes used in this study intentionally treat the plan area and depth as independent variables. Consequently, the mesocosm smallest in volume is not the most shallow of the ponds. These aspects of water body geometry merited close attention because of their potential impact on the initial phase of pesticide behavior. Transfer of chemical from the water column to the benthos takes place across a plane interface, and, consequently, the larger this interface the faster will transfer occur. Similarly, differences in the total volumes of the limnetic and benthic subsystems can have an important effect on the ultimate distribution of pesticide mass between these zones of an aquatic system. For extensively sorbed chemicals, the biota can sometimes act as a significant sink of the material; in this instance we artificially took low biomass values (0.4 mg (dry)/L plankton, 10 mg (dry) m^{-2} benthos) in order to minimize this effect and thus concentrate on some effects of geometry and water/sediment chemistry on pesticide dynamics.

Simulation models

Exposure Analysis Modeling System (EXAMS)

The Exposure Analysis Modeling System (EXAMS, Burns et al. 1982, Burns 1982, 1983, 1990) is an interactive computer-based system for specifying and storing the properties of chemicals and ecosystems, modifying them using simple commands, and conducting rapid evaluations and error analyses of the probable aquatic fate of synthetic organic chemicals. EXAMS constructs simulation models by combining the loadings, transport, and transformations of a chemical into a set of differential equations, using the law of conservation of mass as an accounting principle. This is accomplished by computing the total mass of chemical entering and leaving each section of a body of water as the algebraic sum of external loadings, transport

processes that distribute chemicals through the system and export them across its external boundaries, and transformation processes that convert chemicals to daughter products. The differential equations are then assembled and solved to give a picture of the behavior of chemicals in an aquatic ecosystem. The program produces output tables and graphics that describe chemical exposure, fate, and persistence.

Partitioning to sediments and equilibrium bioconcentration by microplankton and benthos was computed by EXAMS from the octanol:water partition coefficient. EXAMS uses 41% of the KOW as a KOC, and couples the KOC to sediment organic carbon to derive partition coefficients for suspended and bed sediments. The microplankton and benthos partition coefficients (KB) are computed from the relationship developed by Baughman and Paris (1981): log K_B = 0.907 log KOW - 0.361. In this study, we took KOW as 5.2; EXAMS then estimated a log KOC of 4.81 and a log KB of 4.36.

EXAMS computes the kinetics of transformations by direct photolysis, hydrolysis, biolysis, and oxidation reactions; a review of the available literature and preliminary sensitivity analyses using EXAMS suggested that hydrolysis is the dominant dissipative process of fenvalerate in aquatic systems, although the photochemical data are insufficient for a definitive determination. EXAMS' input chemical data can be entered either as single valued, second-order rate constants or as pairs of values defining the rate constant as an Arrhenius function of the temperature in each segment of the water body. An Arrhenius function was used to extrapolate Grayson's hydrolysis data (Table 1) to environmentally relevant temperatures, using the activation energy reported by Camilleri (1984). EXAMS used the vapor pressure and solubility to compute a Henry's Law constant for *fenvalerate*, and a two-resistance model to evaluate the significance of volatilization in our test systems (Burns et al. 1982). Volatilization was unimportant in these systems, and was not explored further.

Pesticide Root Zone Model (PRZM)

Our sensitivity analyses indicated that shallower ponds would more rapidly transfer chemicals from the water column to the bed sediment, suggesting that a case study comparison of the ecotoxicology of shallow mesocosms and farm ponds might illustrate scaling and extrapolation

problems. In constructing our case study, we used "standard evaluation procedures" published by the Office of Pesticide Programs of the U.S. Environmental Protection Agency (Urban and Cook 1986, Touart 1988, Touart and Slimak 1989). We began by positing an application rate of 55 g ai/ha, applied 4 times at intervals of 3 days. This application sums to 220 g ai/ha. Taking 10 percent as the drift from aerial application (Urban and Cook 1986:20), we have a total direct application rate to a farm pond of 22 g ai/ha (spread over 12 days), which if sprayed in a single application would generate a nominal concentration (1.1 µg/L) equivalent to that used for our sensitivity studies.

We then used the "PRZM Input Collator" (PIC, Bird 1990b), a database interface containing soils, crop practices, and meteorological data for PRZM, to select a soil and a meteorological time series for generating agricultural loadings to the farm pond due to runoff from its watershed. PIC selected the Mhoon soil series in Land Resource Region (LRR) "O," the Mississippi Delta Cotton and Feed Grains Region (Soil Conservation Service 1981, Burns et al. 1990), along with a meteorological time series from the "wet" year of 1958 as recorded at Little Rock, Arkansas, as input data for PRZM (Table 5). LRR "O" occupies 116,080 km^2 in the lower Mississippi valley from Louisiana to southern Missouri and Kentucky; the Mhoon soils occupy 33,150 ha in the region. These soils are suitable for cotton, soybeans, wheat, rice, and sugar cane; fenvalerate is effective against pests of all of these crops. The Mhoon soils are sandy loams of hydrologic class D; we instructed PRZM to apply the insecticide on June 1, 4, 7, and 10 (1958) at 55 g ai/ha. We assumed an application efficiency of 60% (i.e., 60% interception by the crop canopy, 40% penetration to the soil surface) and a foliar half-life of about 7.5 days (Willis and McDowell 1987), a soil half-life of 49 days (Williams and Brown 1979), and washoff of 10% per cm of rainfall (Smith and Carsel 1984).

PRZM then produced a time series of per-hectare exports of sediment-bound and waterborne *fenvalerate*; the partitioning among phases was governed by an assumed K_{OC} of 65,000, computed as 41% (Burns et al. 1982) of the octanol:water partition coefficient (log K_{OW} 5.2, Table 1). The Soil Conservation Service (1982) typically recommends a supporting watershed of 2 to 3 acres for every acre-foot of water stored in ponds through much of the Southeast, tending towards a recommended ratio of 4 to 5 acres per acre-foot in much of Land Resource Region "O"

(U.S. Soil Conservation Service 1981). A ratio of two acres to one acre-foot is equivalent to one of 6.56 m^2 of land surface per m^3 of water storage; a one hectare farm pond, 2 meters deep, in Land Resource Region "O" thus would require a minimum watershed area of 13.1 hectares to maintain a year-round water supply. Thus, for each 1958 rainfall event, multiplication of the PRZM per-hectare watershed yields of *fenvalerate* by a factor of 13.1 yielded the pesticide loads entering the farm pond.

The watershed loadings of *fenvalerate* were partitioned between the water column and the benthos of the farm pond by assuming that the sediment-bound materials would sink rapidly to the bottom of the pond and be incorporated into the bottom sediments, while the dissolved loadings would mix into the water column of the pond.

The recommended procedure for mesocosm testing (Touart 1988, Touart and Slimak 1989) is to load the mesocosm with the same concentrations expected from environmental modeling or residue studies. In this case, the volume of the shallow mesocosm is 3.5% of volume of the farm pond (Table 3). Thus, multiplication of the spray drift and watershed erosion loads on the farm pond by a factor of 0.035 served to convert the exposure modeling results to an equivalent time series of loads on the 0.1 ha shallow mesocosm.

RESULTS AND DISCUSSION

Sensitivity analyses of pond types and physical characteristics

Pond Size

Three sizes of ponds, similar in other aspects (nominal properties, Table 4), were compared via the EXAMS model to *fenvalerate* distributions for the first 24 hours after surface introduction, Figs. 1-3.

Water column--The added *fenvalerate* instantaneously distributed to suspended particulate material and plankton, and more slowly distributed to the benthos. Although the quantity added was scaled to have an initial total concentration of 1.0 µg/L in each pond, the initial dissolved concentration was 0.83 µg/L, the remainder being in the particulates and biota (Table 6). In the shallow mesocosm and the small mesocosm, the *fenvalerate* disappeared from the dissolved phase

fairly rapidly, having a half-life of 4 hours in the small, and 2 hours in the shallow, mesocosm. In the farm pond, the half-life was approximately 15 hours (Fig. 1). Assuming that the planktonic organisms were in equilibrium with the dissolved phase, we determined that they initially had concentrations of 18.8 µg/g in all three ponds; the plankton body burden decreased over time as the concentration decreased in the dissolved phase, so that at 24 hours the concentrations in small mesocosm, shallow mesocosm and farm pond were 1.1, 0.23 and 7.6 µg/g (Fig. 2, Table 7).

Sediment--The loss of *fenvalerate* from the water column was almost entirely caused by transfer to the sediment where it distributed to non-living particulates, pore water and benthos. Assuming the benthic organisms were in equilibrium with the benthic pore water, we see that their concentrations increased over time, starting at zero and reaching concentrations about 3 µg/g (Fig. 3). The pond geometry had a major impact on the water:sediment distribution; in the smallest mesocosm and the shallow mesocosm, most was in the sediment (89 and 96% of the initial *fenvalerate* mass), but in the farm pond almost half was still in the water column at 24 hours.

The differences in *fenvalerate* behavior were a direct consequence of the pond size and geometry, as expressed in either area or volume. Because one pond (the "shallow mesocosm") was defined as shallower (0.7 m) than the others (small mesocosm (1 m) or farm pond (2 m)), it has a higher benthic surface: water column volume ratio. The available planar absorptive surface is thus relatively largest in the shallow mesocosm, which consequently loses *fenvalerate* fastest from the water column and initially gains it most quickly in the sediment. If the responses of biota are related to the body burden integrated over time, the plankton in the farm pond should have a much greater response than plankton in smaller, shallower ponds, beyond what might be implied by the differences in concentrations at 24 hours. It is also interesting that the integrated body burdens in the plankton are greater than those of the benthos in all pond sizes, but especially so in the farm pond.

These model results are consistent with, although not identical to, a Canadian model in that *fenvalerate* more rapidly transfers to the sediment in a pond than in a lake (1 m deep, 3.7×10^6 liters, and 15 m deep, 1.0×10^{10} liters, respectively) (Solomon et al. 1986; Roberts et al. 1981). Results should be expected to differ because we used a log Kow (5.2) higher than theirs (4.2).

Physical-Chemical Pond Properties

The effects of varying the properties of the ponds (fraction of organic carbon in the bed sediment, the dispersion coefficient between the water and sediment, and the total suspended material) result in similar curves, but with different initial concentrations (in a few cases) and with very different concentrations at 24 hours. These are summarized in Table 7.

Effects of Organic Content of Sediment

Water Column--The organic content of the sediment (benthic component) proved to have a major effect on the distribution of *fenvalerate* in ponds of all sizes; *fenvalerate* distributes to the sediment more rapidly and to a greater degree in ponds with high organic content in the sediment. The sediment organic content results in differences in the water column at 24 hours of 0.28, 0.049 and 0.004 µg/L in the smallest pond mesocosm. There is a similar 100-fold difference in the shallow mesocosm. In the farm pond, the effect of organic content of the sediment is slightly less; the water column concentration (at 24 hours) is 0.56, 0.33 and 0.061 µg/L for low, nominal and high organic content (1%, 3%, and 10%). The plankton body burdens show the same trends as the dissolved concentration; body burden is greater when organic carbon is lowest.

Sediment--Although higher organic content of the sediment causes *fenvalerate* to distribute to the sediment more rapidly and to a greater degree, the benthos have a lesser body burden with increasing organic carbon in the sediment. The benthos are assumed to be in equilibrium with the benthic pore water; with high organic content, more of the *fenvalerate* is associated with the particulates and less is in the pore water. Comparing the plankton with the benthos, the plankton have greater body burden at 1% and 3% organic carbon sediments, and plankton and benthos have similar body burdens at 10% organic carbon.

Effects of suspended sediment in the water column

Water column--The amount of suspended sediment altered the initial dissolved water concentration because a lesser amount of suspended sediment allowed more *fenvalerate* to be dissolved; this was the only variable tested that altered initial conditions. The initial dissolved concentrations were 0.97 0.83, 0.34 µg/L for low, nominal, and high suspended sediment (3, 30, 200 mg/L) (Table 6). At 24 hours, the differences were most extreme in the small mesocosm; 0.03, 0.04 and 0.10 µg/L

for 3, 30, and 300 mg/L suspended sediments respectively (Table 7). The effects of suspended sediment were less in the larger ponds. These trends were also reflected in the planktonic body burdens, since they are modeled as being in equilibrium with the dissolved phase.

Sediment--The suspended matter in the water column has only slight effects on the amount of *fenvalerate* in the sediment; body burdens of benthos varied only from 0.17 to 0.36 µg/g.

Effects of dispersion coefficient between the water and sediment

Water Column--With a higher dispersion coefficient, *fenvalerate* distributed more rapidly from the water column into the sediment. Differences caused by this variable were 20 fold at the most (in the small pond mesocosm) and of lesser magnitude in the larger ponds. These trends were also reflected in the planktonic body burden (Table 7).

Sediment--The effects on the sediment and benthos were less than 10 fold.

Comparing a shallow mesocosm with high organic sediments and a farm pond with low organic sediments

Water Column--The model outputs proved to be most sensitive to pond geometry and the organic carbon fraction of the sediment. To examine the extremes of output, the farm pond with low organic sediments (1% organic carbon) was contrasted with the shallow mesocosm of high organic sediments (10% organic carbon) (Figs. 4, 5, 6). In the shallow mesocosm, *fenvalerate* disappeared rapidly from the water column, whereas in the farm pond, more than half was still present at 24 hours. The concentrations in the small planktonic organisms paralleled the concentration of dissolved *fenvalerate*, at 0.065 and 1.26 µg/g at 24 hours in the shallow mesocosm and farm pond, respectively.

Sediment--The benthic organisms, initially at zero concentration, initially increase at a much higher rate in the shallow mesocosm than in the farm pond because the mesocosm has a smaller surface:volume ratio, but the concentration in the farm pond benthic organisms is greater at 24 hours; the concentration in the mesocosm benthos (0.0066 µg/g) is less than in the farm pond benthos (4.13 µg/g) in part because the high organic content of the mesocosm sediments competes

with the organisms for *fenvalerate*. In the mesocosms, the plankton and benthos have similar body burdens at 24 hours. In the farm pond, the plankton have a much higher body burden than the benthos (1.2 vs. 0.41 µg), but over longer time periods, the benthos would be expected to increase and the plankton to decrease in body burden.

Results of field-scale exposure analysis and aquatic simulations

The PRZM model produced a total of 34 runoff events between June 11 and December 31, 1958. The largest event occurred on June 25, resulting in a transmission to the farm pond of 3.91 g of *fenvalerate*; this is 0.14% of the total applied in the watershed (four applications of 55 g ai/ha over 13.1 ha, i.e., 2.882 kg total application in the watershed). The total loss from the watershed to the pond was 0.36% of the total application (Table 8). By comparison, Smith et al. (1983) observed a loss of 0.56% of 220 g ai/ha fenvalerate applied to sugarcane during a wet year. The total load to the farm pond and the shallow mesocosm is dominated, however, by the spray drift during application: the pond would receive 5.5 g ai (10% of the application rate) on each of four occasions. The direct (spray drift) application (22 g), when added to the watershed contribution of 10.25 g, gives a total load to the farm pond of 32.25 g *fenvalerate*; 68% of the total load is due to spray drift.

The ecotoxicological consequences of these loadings differ between the shallow mesocosm and the prototype farm pond. The case for a shallow mesocosm with 10% organic carbon content of benthic sediments, versus the farm pond with a 1% organic carbon benthic sediment, is shown in Fig. 7 for *fenvalerate* dissolved in the water column, and in Fig. 8 for the benthic pore water concentrations. Despite scaling the *fenvalerate* inputs to the shallow mesocosm to achieve identical nominal concentration pulses, the systems are very different in terms of their actual organism exposure. At longer times, the integrated exposure of the benthic infauna involves exposures to concentrations exceeding 0.02 µg/L through the end of the year in the farm pond, while exposures in the shallow, organic-rich mesocosm never exceed 0.005 µg/L in the sediment pore water (Fig. 8).

We used EXAMS' reporting facilities to bring out these contrasts in more detail. Table 9 gives, for the shallow mesocosm and farm pond of high (10%) and low (1%) organic carbon, the

exposure concentrations in the water column resulting from the fourth spray drift event (June 10 "1958"), exposures 24 hours later (June 11), and exposures resulting from the rainfall/runoff event of 11 June. Although the concentrations resulting from the final spray drift event are roughly comparable, within 24 hours the systems diverge. There is a significant effect of size alone: at the end of 24 hours the shallow mesocosm and farm pond with low organic carbon differ by a factor of 5 (0.048 µg/L in the shallow mesocosm, 0.24 µg/L in the farm pond); in the organic-rich systems they differ by a factor of 7 (0.071 µg/L versus 0.52 µg/L). As a consequence of these differing base lines, the erosion of *fenvalerate* from the watershed has differing impacts: the organic-rich shallow mesocosm is the only system that experiences a significant increase in exposure (from 0.0032 µg/L to 0.011 µg/L) due to erosion of contaminated field soil from rainfall. The effect of differing organic matter content is even greater: both the shallow mesocosm and the farm pond experience exposures at the end of 24 hours (June 11) that differ by more than an order of magnitude (e.g., 0.24 µg/L versus 0.023 µg/L in the farm pond). Across our primary comparison--the shallow mesocosm with 10% organic C versus the farm pond with 1% organic C--the exposure concentration differs by a factor of 75 (0.0032 µg/L versus 0.24 µg/L); the organic-rich sediments in the shallow mesocosm reduce the potential toxicity by nearly two orders of magnitude.

At longer times, the shallow mesocosm and the farm pond differ less, at least when only size effects are considered. In Table 10 we have summarized the outputs produced by the EXAMS program running in its annual simulation mode to simulate the field use scenarios. The values reported in this table represent the largest toxicity events of 96-hour or 21-day duration, and the concentrations averaged over the entire year of study (including the zero values prior to the first spray event of June 1 in the long-term average). In general, size effects alone amount to about a factor-of-two difference in exposures of planktonic organisms, with only minor effects on exposure of the benthos. The exposure of planktonic organisms in the farm pond with 1% organic carbon is three to five times larger than that in the other systems, although the long-term exposure of planktonic organisms in the 0.1 ha shallow mesocosm is reduced by 4× in the high organic carbon system.

The largest differences among systems are found in the exposure of the benthos. The combination of substantial size and organic carbon effects on exposure patterns results in massive differences in the exposure experience of the benthos in the 0.1 ha test system and the 1.0 ha prototype. The 96-hour exposure differs by 16× (0.0043 µg/L of pore water in the 10% organic carbon shallow mesocosm, versus 0.069 µg/L in the pore water of the 1% organic carbon farm pond), the 21 day exposure differs by 15×, and the long-term exposure differs by 10× (Table 10). These exposures are mirrored in the computed body burden for small benthic organisms; thus both the food-chain exposure and the physical exposure of the macrobenthos would differ by an order of magnitude between the shallow mesocosm and the farm pond.

Effects of chemical properties

In the longer-term simulation studies, hydrolytic decomposition of the parent *fenvalerate* is clearly discernible, as seen, for example, in the time-traces of dissolved concentrations (Figs. 8 and 9). Hydrolysis of the ester bond appears to be the primary decomposition pathway of *fenvalerate*; fenvalerate has been demonstrated to undergo base-catalyzed decomposition (Camilleri 1984). Solomon et al. (1986) give pseudo-first-order hydrolysis rate constants of 7.28×10^{-4} day^{-1} (at pH 6) and 7.38×10^{-3} day^{-1} (at pH 8) for environmental modeling; the values listed in Table 1 have been calculated from these data and used in our simulations (Fig. 8 and 9).

Camilleri (1984) determined the activation energy of the base-catalyzed hydrolysis of fenvalerate to be 12 kcal/mole, a value typical of this type of reaction (Kirby 1972). When this value (12 kcal/mole) is used to extrapolate Grayson's (1975, Table 1) results to 25°C., the result is a K_{OH} of 492 $h^{-1}M^{-1}$, which compares favorably with Camilleri's measured K_{OH} of 520 $h^{-1}M^{-1}$ (Table 1). The contrasting results obtained with these competing estimates of the hydrolytic lability of fenvalerate are shown in Table 11. The half-lives given in this table are computed from the ratio of the hydrolytic flux to the total *fenvalerate* in the system; transport effects are neglected. Thus, the shortest estimated half-life is that for the low organic carbon farm pond, primarily because more of the *fenvalerate* remains in the water column and is available to the more alkaline (pH 8) conditions in the water column. In using the values of Solomon et al. (1986), we made the typical assumption that dissolved *fenvalerate* is available for hydrolytic reaction, and sorbed material is unavailable. Recent work (Wolfe 1990) has indicated that neutral

hydrolysis (pH-independent attack by the water molecule) is not affected by the sorbed state, whereas alkaline hydrolysis is drastically diminished. We used this set of assumptions to drive the second series of simulations. Thus, hydrolysis half-lives (Table 11) computed using an Arrhenius function (Table 1) also assume that neutral hydrolysis proceeds at the same rate regardless of sorption to organic matter. Note that the interaction of pond geometry and organic carbon content of the benthic sediment is again apparent, under both sets of assumptions. In all cases, the low organic carbon farm pond dissipates *fenvalerate* faster than any other case. These results are in accord with the observation (Williams and Brown 1979) that fenvalerate tends to persist from year to year in highly organic soils. The tendency of highly organic systems to retain the material for extended periods implies that multi-year use of this insecticide could begin to show frank toxicity during the second or third year of use. It also implies that the sediments of mesocosms require careful analysis for persistent residues if they are to be used in successive years for ecotoxicological investigation of different chemicals.

CONCLUSIONS

Sensitivity analysis of dissolved, surface inputs

Even when initial water concentrations are similar, geometry and physical and chemical properties of the aquatic environment can cause toxicologically significant differences in the exposure of organisms. Large surface:volume ratios promote transfer from the water column to benthic zones or the atmosphere; a shallow mesocosm can under-represent the ecotoxicological duration of exposures in a larger farm pond; a deeper mesocosm behaves more like the farm pond. Strongly sorbing chemicals are taken up in large quantities by plankton during the initial phases of exposure and remain significant despite transfer of the bulk of the contaminant to the benthic sediment. Over time, the benthos and plankton exposures converge; the ecotoxicological consequences then depend on differential organism sensitivities. Sediment organic carbon acts as a sink for pesticide contamination, both promoting transfer to the benthic zone and minimizing the amount dissolved in benthic pore water, thus protecting benthos from direct exposures. However, organisms feeding on benthic particulate matter will experience a more contaminated food. Suspended particulates reduce dissolved concentrations and thereby protect organisms from direct exposure. A larger empirical dispersion coefficient (linking water column and benthic zone) speeded transfer of chemical between these subsystems. Pond geometry and organic carbon

content of benthic sediments produced the greatest differences between exposures (Figs. 4-6). The other systems gave results intermediate between these extremes. In the (1% organic carbon sediment) farm pond, both the plankton and the benthos are exposed to longer periods of higher concentrations of *fenvalerate*, and accumulate greater body burdens than in the shallow mesocosm.

In sum, the sensitivity analyses indicate that very different exposure could be experienced by organisms in ponds of different sizes and characteristics, even if initial concentrations of *fenvalerate* in the surface water were 1.0 µg/L in each case. If the biological responses are related to the integrated body burdens (body burden x duration), then the organisms in a shallow mesocosm would be expected to have much lesser response than those experienced by organisms in deeper mesocosms or farm ponds.

Agricultural applications

A moderate agricultural use scenario included four spray drift events (dissolved surface input of 10% of the 55 g ai/ha application rate) and 34 rainfall/runoff events (partially dissolved and partially on soil particulates). Spray drift was 0.76%, and watershed erosion 0.36%, of the total applied in the watershed, in satisfactory agreement with results of field investigations (Smith et al. 1983). The pond inputs were scaled to give similar (1.1 µg/L) initial concentrations in the mesocosm. Application of these realistic (spray drift plus erosion) loading scenarios to this farm pond (1% sediment organic carbon) and shallow mesocosm (10% sediment organic carbon) gave organism exposures and body burdens 5 to 75 times higher in the farm pond than in the shallow mesocosm (Figs. 7, 8). Thus, mesocosms require thoughtful analysis and extrapolation to the larger-scale aquatic ecosystems of which they are a physical model; they are not a complete experimental substitute for ecological analysis and risk assessment.

Chemical properties

We find, with others (e.g., Solomon et al. 1986) that the chemical database available for ecotoxicological mathematics is replete with uncertainties and depauperate in incontrovertibly valid and appropriate studies. Here, the investigations of fenvalerate hydrolysis are flawed (for our purposes) by having been conducted at elevated temperatures and in non-aqueous solvent systems. As a result, diametrically opposed conclusions as to fenvalerate persistence are possible,

with little basis for incontrovertible choice between them. Major uncertainty in KOW, although we do not report results here, could induce differences at least as large as those resulting from differences in organic carbon content of sediments. A higher KOW would have resulted in faster transfer from the water column to the benthos, as well as more extensive contamination of bed sediments. Alkali-catalyzed rupture of the ester bond is the primary decomposition pathway of fenvalerate. Because the open water pH is 8, and the benthic pore water pH is 6, the half-life in the larger farm pond is always shorter than in the shallow mesocosm. In addition, the more organic-rich systems sequester the insecticide and extend the half-life to a year or more. Differences in reported hydrolysis studies lead to major differences in projected half-lives with potential year-to-year accumulation in both the farm pond and the shallow mesocosm.

The results of these model exercises suggest caution in using mesocosms as physical models for the protection of all aquatic communities, unless exposures are appropriately scaled and suitable measures are taken to allow for both physical and chemical differences. Certainly, with the parameters used in these models, chemicals that have relatively low exposures in shallow, eutrophic mesocosms could have much greater exposures in deeper, more mesotrophic ponds with sediments of lower organic carbon.

To place these exposure concentrations in the context of potential toxicity, Table 12 provides a survey of toxicity data. *Daphnia* acute toxicities have been reported in the range of 0.3-10.25 µg/L 24 hr EC_{50} (depending on species and size) whereas decreased *Daphnia* filtering has been reported to occur at concentrations of 0.05 µg/L (Day and Kaushik 1987). The copepod *Diaptomus oregonensis* was less sensitive and did not show filtering inhibition at concentrations of 0.1 µg/L, but did show filtering inhibition at 0.5 µg/L.

Trophic interactions also influence the responses of aquatic communities to pesticides. A major review of the seasonal succession of ponds, lakes and reservoirs described predictable shifts in the factors controlling algal and zooplankton standing crops, as well as the exceptions to the general patterns (Sommer et al. 1986, Lampert 1987). In most temperate aquatic communities, the spring algal bloom is terminated by the combined effects of zooplankton grazing and nutrient depletion, resulting in a temporary "clear period." During the period when zooplankton grazing is

controlling the algal biomass, an insecticide that markedly reduces zooplankton density is likely to result in a phytoplankton bloom. Later in the season, the phytoplankton escape zooplankton control, either (1) because the algal dominance shifts to species difficult for zooplankton to consume (because of size or gelatinous sheaths), (2) because fish predation reduces the abundance of zooplankton (McQueen and Post 1988), or (3) high temperature kills many zooplankton (LaPoint, personal communication). During this second phase, reduction of zooplankton abundance by an insecticide may not cause an increase in phytoplankton abundance. These "clear water phase" patterns were most marked in stratified mesotrophic and eutrophic communities. Exceptions to this general pattern were seen in some lakes that were oligotrophic, or where other factors such as light availability or nutrient recycling exerted greater direct control on phytoplankton production than did grazing (Sommer et al. 1986). We are actively seeking data from pesticide studies that address the effects of pesticide treatment during periods when zooplankton do or do not control phytoplankton abundance.

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TABLE 1. CHEMICAL PROPERTIES OF *FENVALERATE*

Chemical Property	Numerical Value[1]	Source
Molecular Weight (g/mole)	419.9*	Empirical formula
Solubility (µg/L)	0.085* 0.024	Coats and O'Donnell-Jeffrey 1979 Schimmel et al. 1983
Octanol:water partition coefficient (log Kow)	4.42 5.01 5.2*±0.6 6.2	Coats and O'Donnell-Jeffrey 1979 Yoshioka 1979 Muir et al. 1985 Schimmel et al. 1983
Alkaline hydrolysis K_{OH}, $M^{-1}h^{-1}$	6,720* (estimate from Grayson 1975) 8,950 (at 75°C) 540 (at 25°C, in 1:1 dioxane:water)	Solomon et al. 1986 Grayson 1975 Camilleri 1984
Neutral hydrolysis K_N, h^{-1}	6.61×10^{-4}* (estimate from Grayson 1975) 8.81×10^{-4} (at 75°C)	Solomon et al. 1986 Grayson 1975
Hydrolysis activation energy, Ea, kcal $mole^{-1}$	12.* (in 1:1 dioxane:water)	Camilleri 1984
Pre-exponential factor, K_{OH}	11.48*	Calculated from Grayson 1975
Pre-exponential factor, K_N	4.51*	Calculated from Grayson 1975
Vapor pressure (torr)	2.8×10^{-7}*	Yoshioka 1979

[1] Marked (*) values used in simulation studies.

TABLE 2. FARM PONDS OF THE SOUTHEASTERN REGION

	Physiographic Province				
	Mountain	Piedmont	Upper Coastal	Lower Coastal	Total
Total Number	259	11,387	18,258	3,109	33,013
Average Size (ha)	0.61	1.0	1.5	2.0	1.4
Land area (km^2)	3,258	46,988	122,520	51,380	224,150
Ponds per km^2	0.08	0.24	0.15	0.06	0.15
Type of Water Use	Percent of total (total exceeds 100% due to multiple use)				
Farmstead	34	48	45	69	48
Irrigation	4	3	13	54	13
Fish Management	75	86	71	71	76

TABLE 3. CONSTANT PROPERTIES OF SIMULATED PONDS

Property	Small Mesocosm	Shallow Mesocosm	Farm Pond
Plan area (m^2)	25.	1000.	10,000.
Volume (m^3)	25.	700.	20,000.
Water depth (m)	1.0	0.7	2.0
Water column pH	8.0	8.0	8.0
Sediment pH	6.0	6.0	6.0
Benthic interface (m^2)	25.[1]	1090.[2]	10,400.[2]
Active sediment depth (cm)	2.5	2.5	2.5
Sediment water content (%)	137.	137.	137.
Sediment bulk density (g/cm^3)	1.85	1.85	1.85

[1] Neglecting concrete non-sorptive side walls

[2] Assuming vertical side walls and rectangular plan.

TABLE 4. CHEMICAL AND PHYSICAL PROPERTIES VARIED IN SENSITIVITY TESTS

Property	Low	Nominal	High
Suspended Sediment (mg/L)	3.0	30.	300.
Dispersivity (m^2 hr^{-1})	$1.0x10^{-5}$	$2.8x10^{-5}$	$7.5x10^{-5}$
Benthic Organic Carbon (%)	1.	3.	10.

TABLE 5. PROPERTIES OF MHOON SOILS

Layer	Depth (cm)	Bulk density (g/cm^3)	Organic Carbon (%)
Surface	15	1.65	0.29
Sub-surface	135	1.70	0.174

TABLE 6. INITIAL CHEMICAL DISTRIBUTION IN SIMULATED PONDS

	Water Column Dissolved Concentr. µg/L	Water Column Total Mass grams
Effects of Geometry, Nominal Conditions		
Small Mesocosm	0.831	0.025
Shallow Mesocosm	0.831	0.70
Farm Pond	0.831	20.0
Effects of Suspended Matter in Water Column		
Small Mesocosm (0.0025 ha)		
Low (3 mg/L)	0.972	0.025
Nominal (30 mg/L)	0.831	0.025
High (300 mg/L)	0.338	0.025
Shallow Mesocosm (0.1 ha)		
Low (3 mg/L)	0.972	0.70
Nominal (30 mg/L)	0.831	0.70
High (300 mg/L)	0.338	0.70
Farm Pond (1 ha)		
Low (3 mg/L)	0.972	20.0
Nominal (30 mg/L)	0.831	20.0
High (300 mg/L)	0.338	20.0

TABLE 7. 24-HOUR CHEMICAL DISTRIBUTION IN SIMULATED PONDS 1

	Water Column		Benthic		Water Column	Benthic
	Dissolved Concen. µg/L	Total mass grams	Total mass grams	Total Concentration µg/kg	Body Burden µg/g	Body Burden µg/g
Effects of size alone; nominal conditions of other parameters						
Small Mesocosm	0.050	0.0015	0.022	26.4	1.12	0.308
Shallow Mesocosm	0.010	0.0087	0.675	18.3	0.233	0.213
Farm Pond	0.337	8.12	9.93	28.3	7.64	0.329
Effects of organic carbon in benthic sediment						
Small Mesocosm						
Low	0.281	0.0085	0.014	16.9	6.37	0.591
Nominal	0.050	0.0015	0.022	26.4	1.13	0.308
High	0.004	0.0001	0.024	29.0	0.101	0.101
0.1 ha Shallow Mesocosm						
Low	0.101	0.0849	0.573	15.6	2.28	0.543
Nominal	0.010	0.0087	0.675	18.3	0.233	0.213
High	0.003	0.0024	0.692	18.8	0.065	0.066
1 ha Farm Pond						
Low	0.557	13.4	4.16	11.8	12.6	0.413
Nominal	0.337	8.12	9.93	28.3	7.64	0.329
High	0.061	1.48	17.5	49.8	1.39	0.174

TABLE 7. 24-HOUR CHEMICAL DISTRIBUTION IN SIMULATED PONDS 2

	Water Column		Benthic		Water Column	Benthic
	Dissolved Concen. µg/L	Total mass grams	Total mass grams	Total Concentration µg/kg	Body Burden µg/g	Body Burden µg/g
Effects of suspended matter in the water column						
Small Mesocosm						
Low	0.039	0.0010	0.023	27.0	0.878	0.314
Nominal	0.050	0.0015	0.022	26.4	1.13	0.308
High	0.102	0.0075	0.017	19.7	2.31	0.229
0.1 ha Shallow Mesocosm						
Low	0.010	0.0069	0.676	18.4	0.218	0.214
Nominal	0.010	0.0087	0.675	18.3	0.233	0.213
High	0.030	0.0623	0.622	16.9	0.682	0.197
1.0 ha Farm pond						
Low	0.339	6.97	10.9	31.0	7.68	0.361
Nominal	0.337	8.12	9.93	28.3	7.64	0.329
High	0.234	13.8	5.15	14.7	5.30	0.171

TABLE 7. 24-HOUR CHEMICAL DISTRIBUTION IN SIMULATED PONDS 3

	Water Column		Benthic		Water Column	Benthic
	Dissolved Concen. µg/L	Total mass grams	Total mass grams	Total Concentration µg/kg	Body Burden µg/g	Body Burden µg/g
Effects of benthic:limnetic dispersion (mixing) coefficient						
Small Mesocosm						
Low	0.261	0.0078	0.015	17.7	5.91	0.206
Nominal	0.050	0.0015	0.022	26.4	1.13	0.308
High	0.015	0.0004	0.02、	28.5	0.331	0.331
0.1 ha Shallow Mesocosm						
Low	0.081	0.0681	0.592	16.1	1.83	0.187
Nominal	0.010	0.0087	0.675	18.3	0.233	0.213
High	0.009	0.0080	0.685	18.6	0.214	0.217
1.0 ha Farm Pond						
Low	0.548	13.2	4.39	12.4	12.4	0.145
Nominal	0.337	8.12	9.93	28.3	7.64	0.329
High	0.111	2.66	16.1	45.8	2.51	0.534

TABLE 8. POND LOADS FROM AGRICULTURAL FIELD SPRAYING AND RUNOFF/EROSION

	grams *fenvalerate*	percentage
Watershed application	2882.	100.0
Spray drift to pond	22.0	0.76
Watershed runoff and erosion	10.25	0.36
Total load to farm pond	32.25	1.12

TABLE 9. SHORT-TERM EXPOSURE IN AGRICULTURAL FIELD-USE SCENARIO

Ecosystem Plan area	Shallow Mesocosm 0.1 ha	Farm Pond 1.0 ha	Shallow Mesocosm 0.1 ha	Farm Pond 1.0 ha	Shallow Mesocosm 0.1 ha	Farm Pond 0.1 ha
Date Event	6/10/58 Spray Drift	6/10/58 Spray Drift	6/11/58	6/11/58	6/11/58 Rainfall	6/11/58 Rainfall
Low (1%) Organic Carbon						
Dissolved (µg/L)	0.25	0.34	0.048	0.24	0.055	0.24
Plankton (mg/kg)	5.6	7.7	1.1	5.3	1.2	5.5
High (10%) Organic Carbon						
Dissolved (µg/L)	0.23	0.23	0.0032	0.023	0.011	0.031
Plankton (mg/kg)	5.2	5.3	0.071	0.52	0.25	0.70

TABLE 10. LONG-TERM EXPOSURE IN AGRICULTURAL FIELD-USE SCENARIO

Ecosystem Plan area	Shallow Mesocosm 0.1 ha	Farm Pond 1.0 ha	Shallow Mesocosm 0.1 ha	Farm Pond 1.0 ha	Shallow Mesocosm 0.1 ha	Farm Pond 1.0 ha
Interval	96-h	96-h	21-d	21-d	1958	1958
Low (1%) Organic Carbon						
Water Col. Dissolved (µg/L)	0.086	0.22	0.047	0.13	0.018	0.024
Plankton (µg/g)	1.9	5.0	1.1	3.0	0.40	0.55
Benthic Dissolved (µg/L)	0.034	0.069	0.034	0.066	0.016	0.025
Benthos (µg/g)	0.77	1.6	0.76	1.5	0.36	0.56
High (10%) Organic Carbon						
Water Col. Dissolved (µg/L)	0.059	0.069	0.026	0.032	0.0049	0.0088
Plankton (µg/g)	1.4	1.6	0.56	0.72	0.11	0.20
Benthic Dissolved (µg/L)	0.0043	0.011	0.0043	0.011	0.0025	0.0065
Benthos (µg/g)	0.099	0.26	0.098	0.26	0.057	0.15

TABLE 11. HALF-LIFE OF *FENVALERATE* (MONTHS) AS A FUNCTION OF HYDROLYSIS RATE

	SOLOMON ET AL. 1986		CAMILLERI 1984	
Ecosystem Plan area	Shallow Mesocosm 0.1 ha	Farm Pond 1.0 ha	Shallow Mesocosm 0.1 ha	Farm Pond 1.0 ha
Low (1%) Organic Carbon	4.5	1.8	19.	13.
High (10%) Organic Carbon	25.	12.	24.	23.

TABLE 12. FENVALERATE INVERTEBRATE TOXICITY

(Day and Kaushik 1987, Day 1989)

Exposure (µg/L)	Taxon	Effect
6.58	*Daphnia magna* adult	24-h EC_{50} (Immobilization)
1.80	*Daphnia magna* <48 hr old	24-h EC_{50} (Immobilization)
1.09	*Ceriodaphnia lacustris*	24-h EC_{50} (Immobilization)
0.50	*Daphnia galeata mendotae*	24-h EC_{50} (Immobilization)
0.49	*D. galatea mendotae* <48 hr old	24-h EC_{50} (Immobilization)
0.25	*Diaptomus oregonensis* adult	24-h EC_{50} (Immobilization)
0.05	*Daphnia galeata mendotae*	Decreased filtration rate
0.01	*Ceriodaphnia lacustris*	Decreased filtration rate
0.005	*Daphnia galeata mendotae*	Reduced longevity, number of broods, and brood size

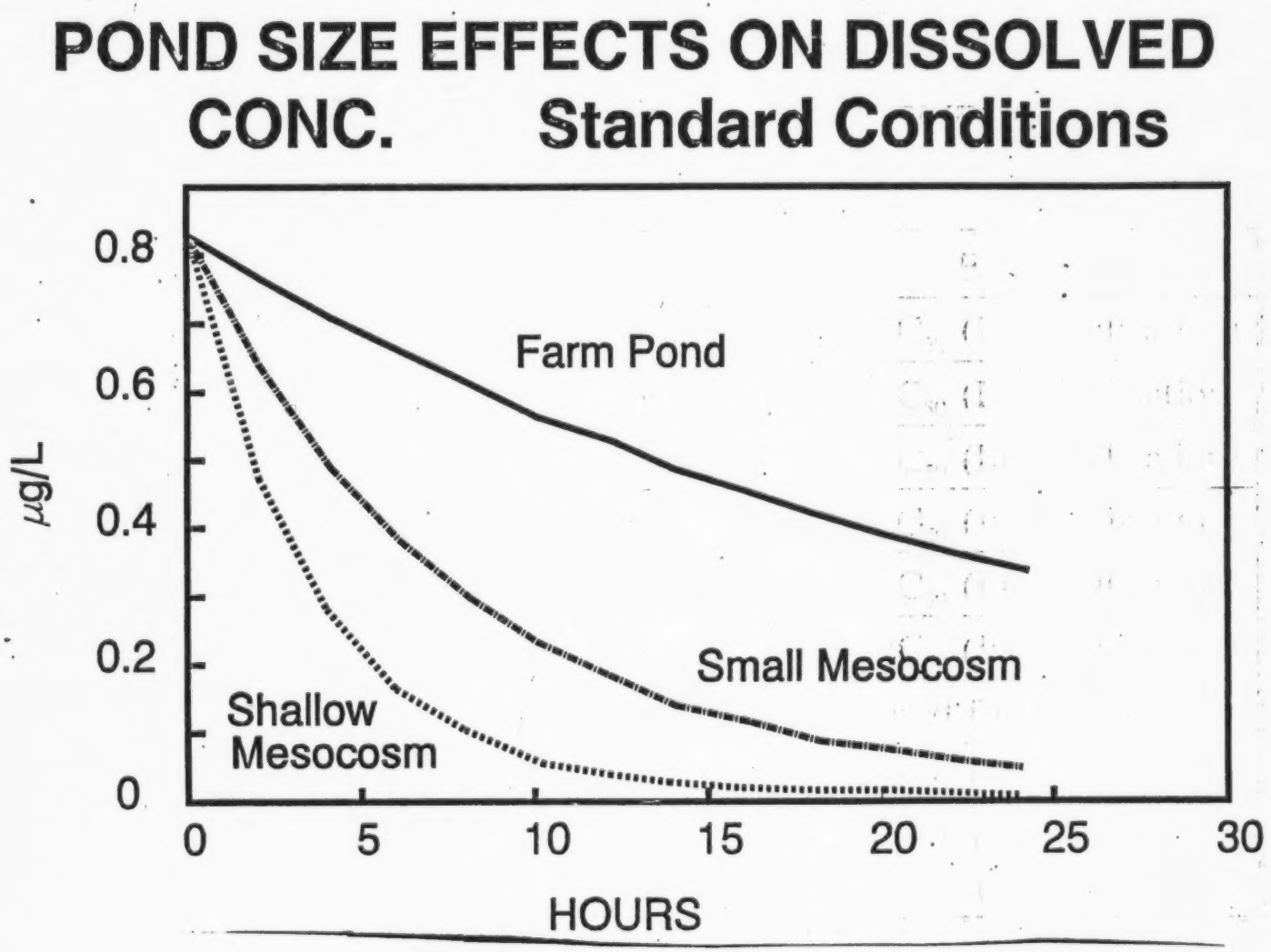

Figure 1. Sensitivity analysis of pond geometry on initial exposure. The "shallow mesocosm" is not the smallest system, illustrating the importance of surface:volume ratio rather than size per se.

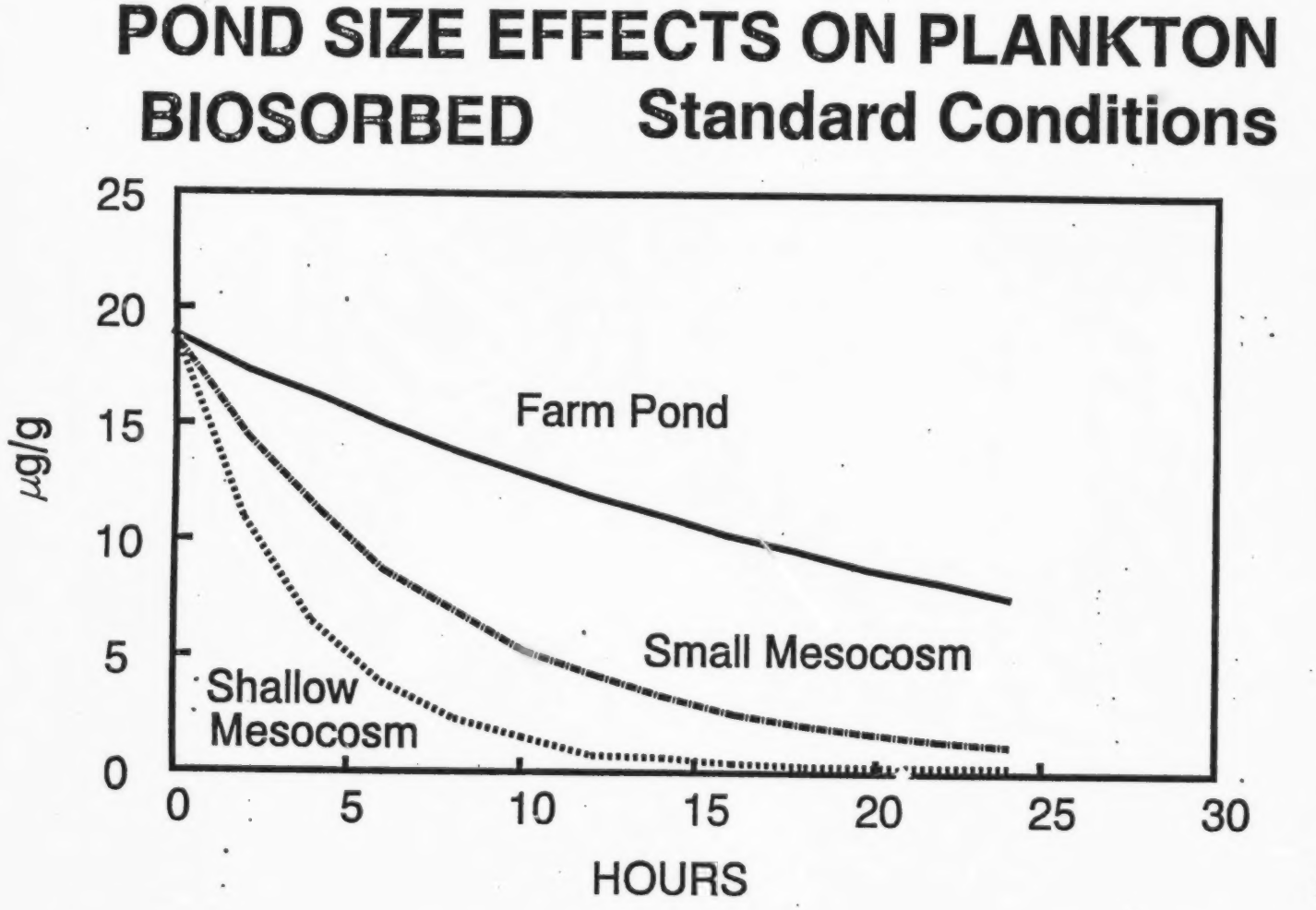

Figure 2. Effects of pond geometry on exposure, as expressed by contamination of microplankton assuming rapid equilibrium partitioning.

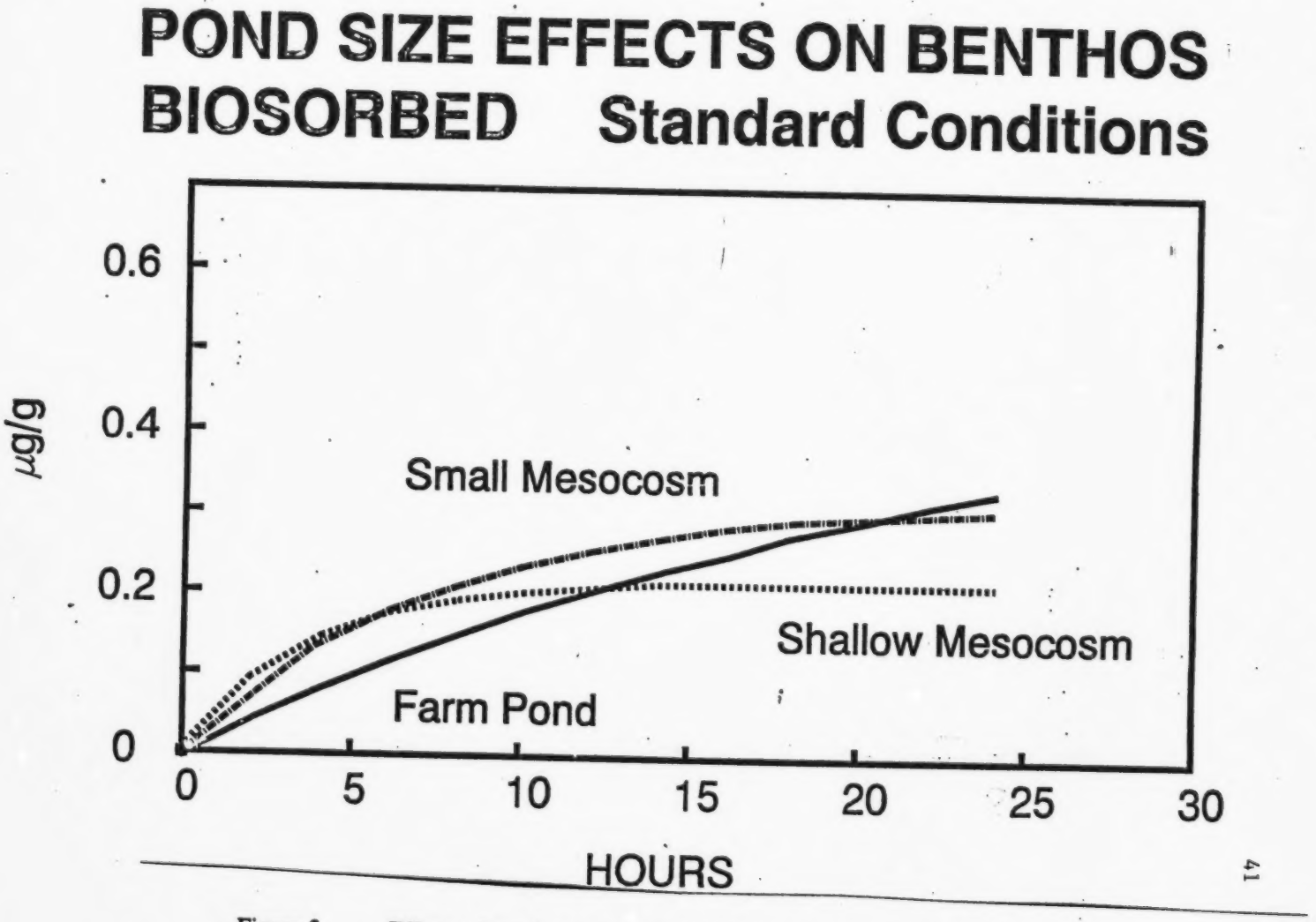

Figure 3. Effects of pond geometry on initial body burden of microbenthos.

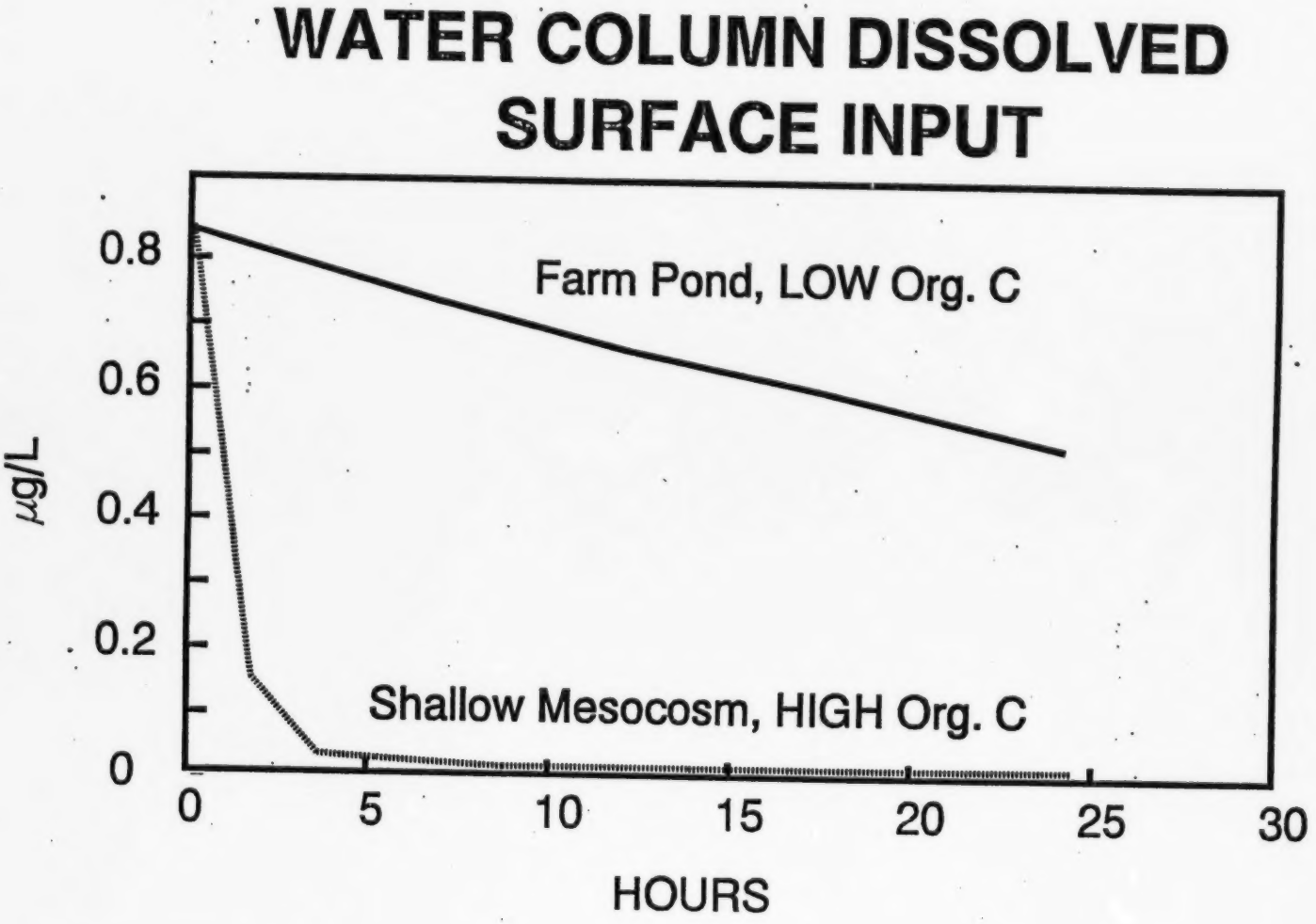

Figure 4. Sensitivity comparison of high organic shallow mesocosm with less eutrophic, deeper farm pond: dissolved concentrations in the water column.

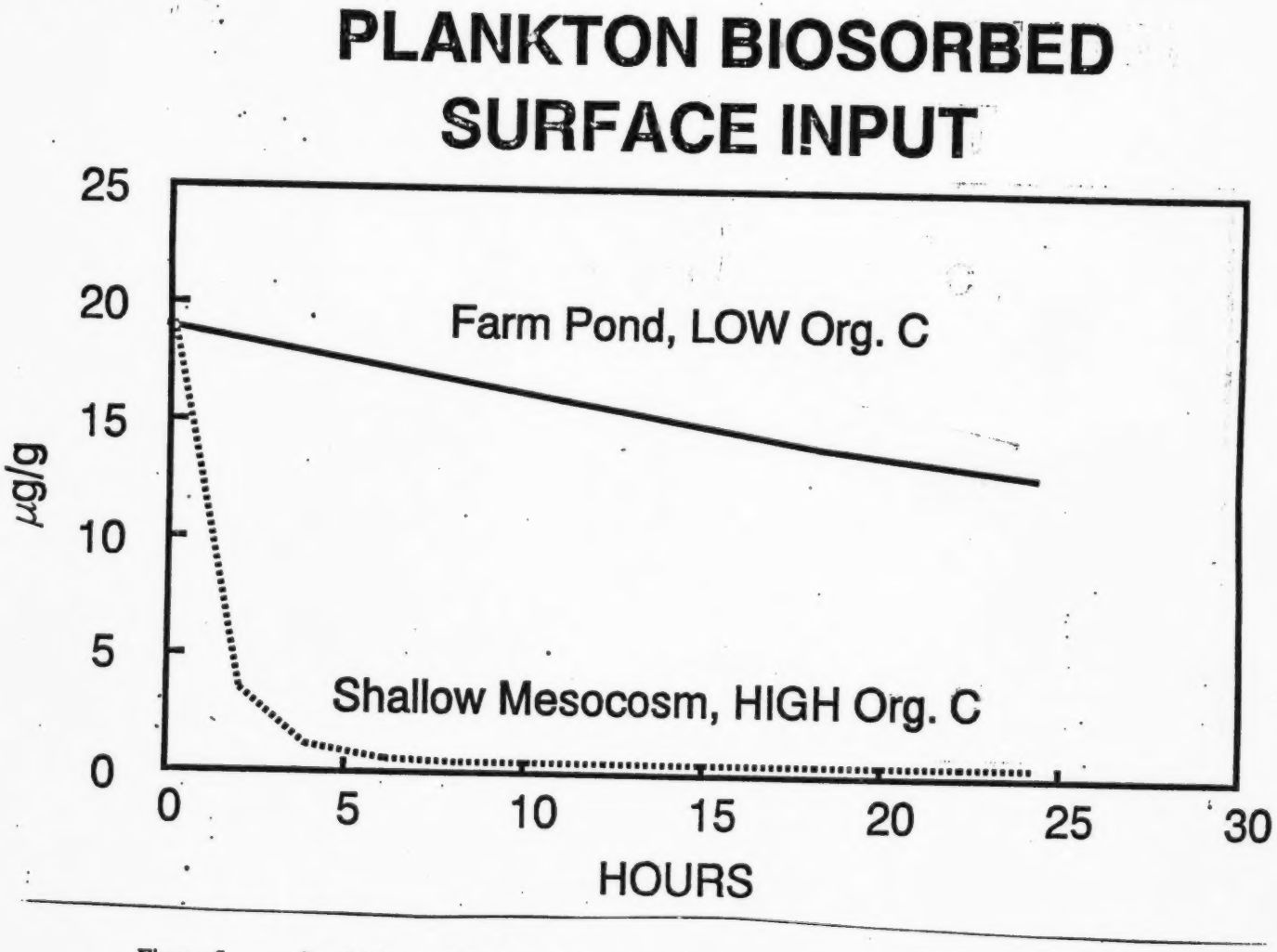

Figure 5. Sensitivity comparison of high organic shallow mesocosm with less eutrophic, deeper farm pond: contamination of microplankton.

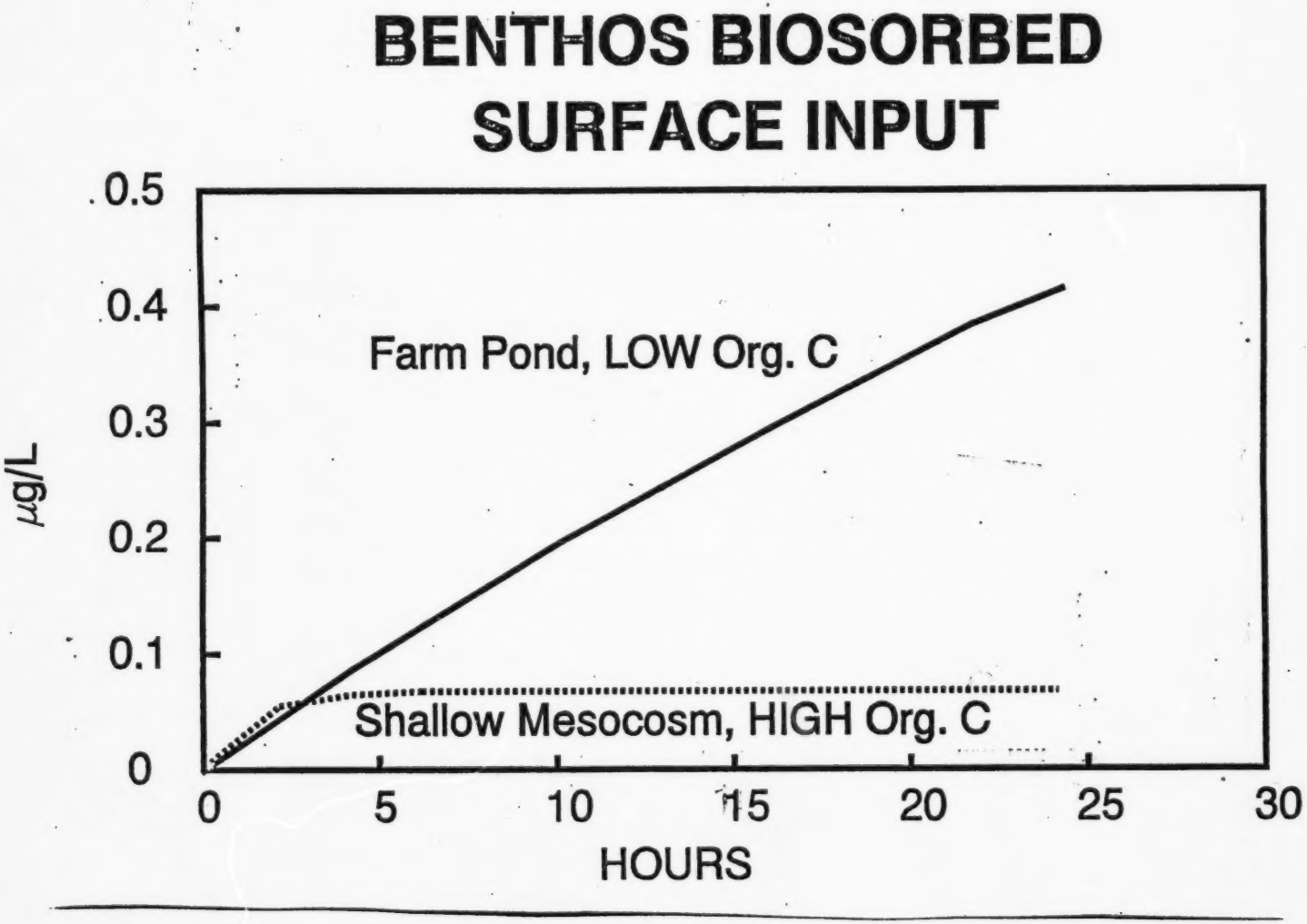

Figure 6. Sensitivity comparison of high organic shallow mesocosm with less eutrophic, deeper farm pond: contamination of microbenthos.

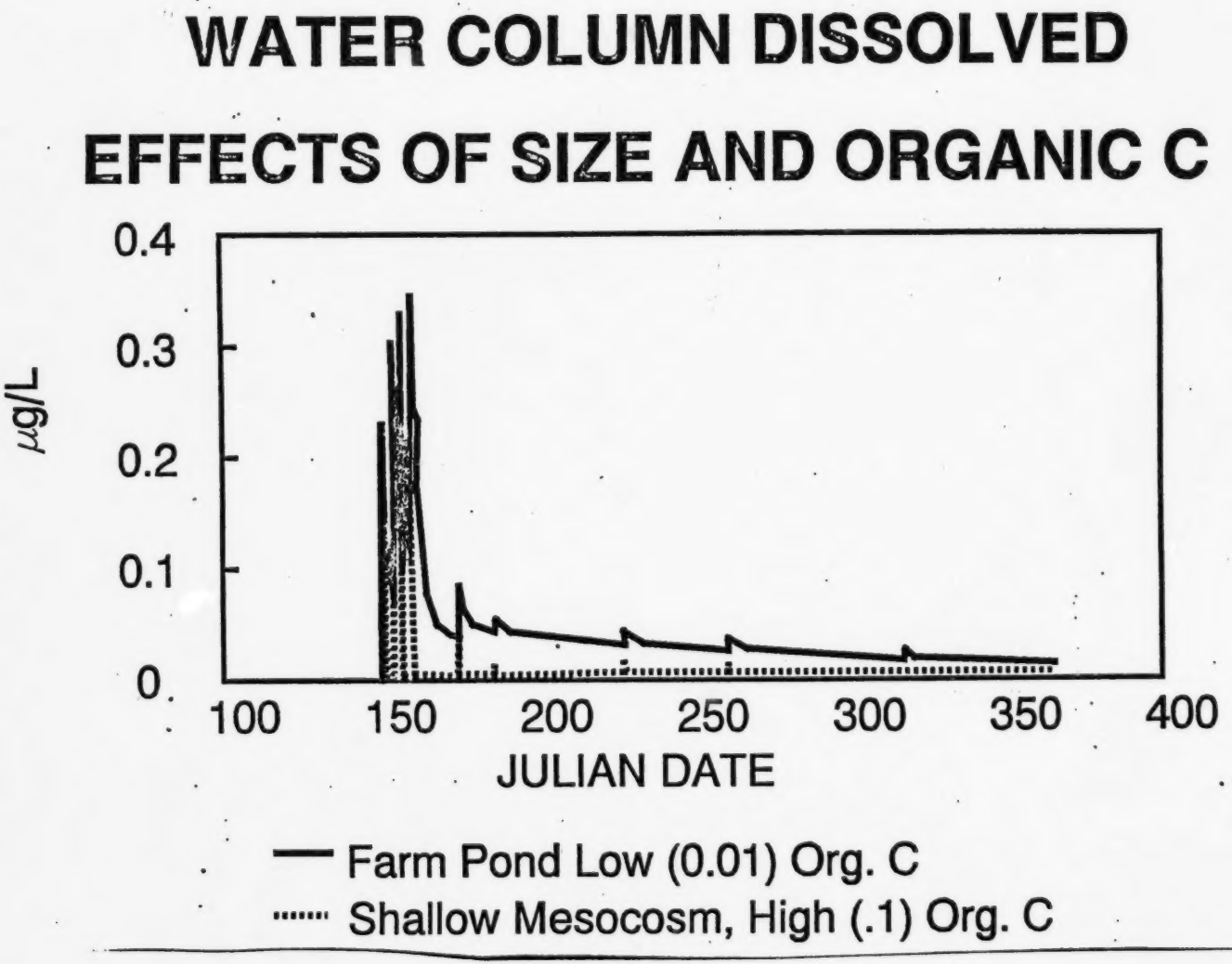

Figure 7. Comparison of dissolved *fenvalerate* in surface waters of shallow mesocosm and farm pond receiving spray drift and erosion from agricultural watershed.

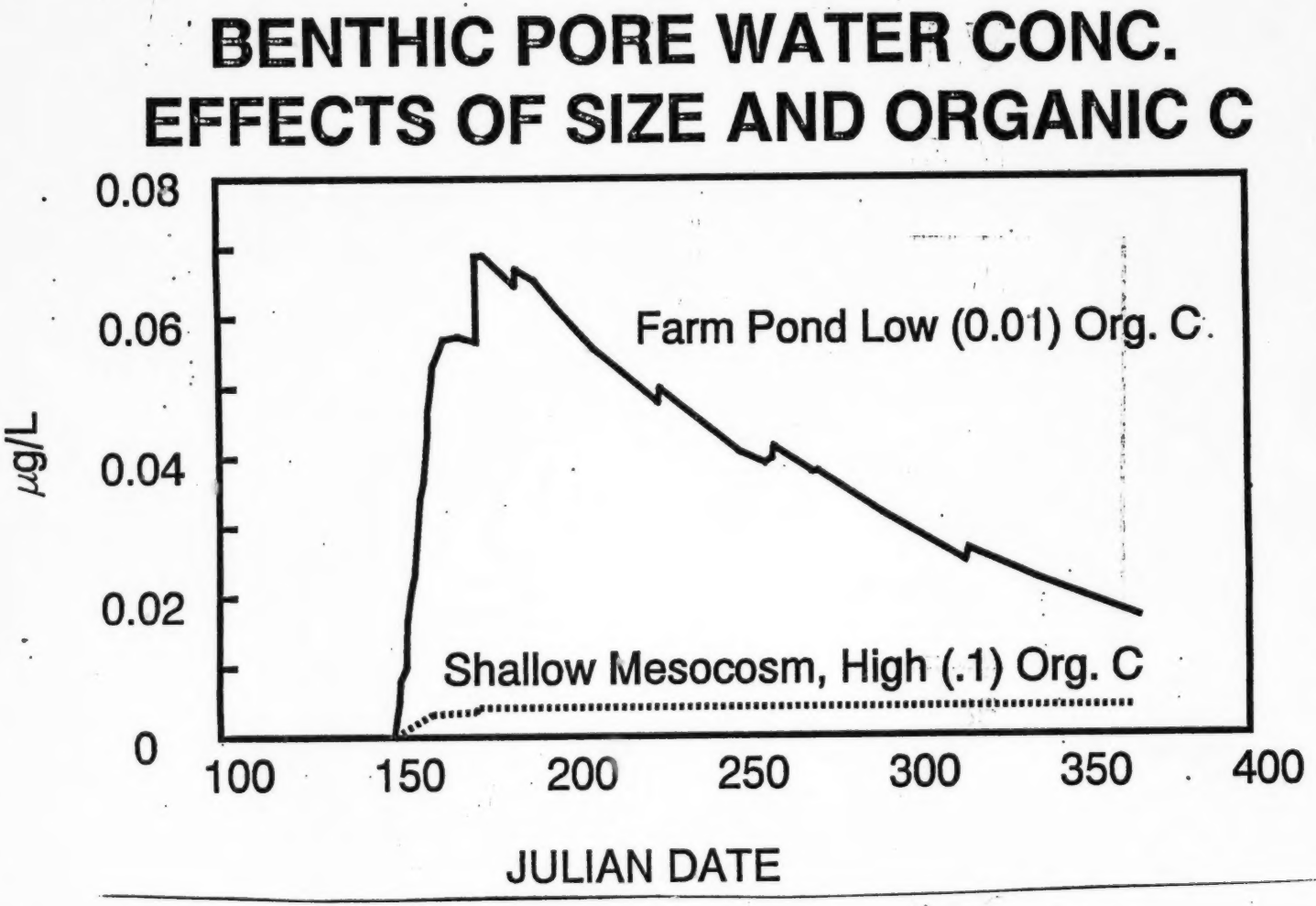

Figure 8. Comparison of dissolved *fenvalerate* in benthic interstitial water of shallow mesocosm and farm pond receiving spray drift and erosion from agricultural watershed.